SELENIUM AND THE SALTON SEA

WHAT IS SELENIUM?

(Pronounced se lee'nee-um) Selenium is a semi-metallic naturally occurring trace element. It is widely but unevenly distributed as a solid substance in the earth's crust. It is commonly found in rocks and soil. Selenium, in its pure form of metallic gray to black hexagonal crystals, is often referred to as elemental selenium or selenium dust. However, in the environment, selenium is not often found in this pure form. Much of the selenium in rocks is combined with sulfide minerals or with silver, copper, lead, and nickel minerals.

Most processed selenium is used in the electronics industry, but it is also used: as a nutritional supplement; in the glass industry; as a component of pigments in plastics, paints, enamels, inks, and rubber; in the preparation of pharmaceuticals; as a nutritional feed additive for poultry and livestock; in pesticide formulations; in rubber production; as an ingredient in antidandruff shampoos; and as a constituent of fungicides. Radioactive selenium is used in diagnostic medicine.

WHY SELENIUM IS IMPORTANT

Selenium tends to be present in large amounts in areas where soils were derived from Cretaceous and Tertiary marine sedimentary rocks. Selenium from these sources is highly mobile and biologically available in arid regions having alkaline soils. When these formations are modified as a result of human activities (e.g. agricultural irrigation), the selenium may be mobilized and become more available to plants and animals, which bioaccumulate selenium and incorporate it into the food chain for other organisms. Selenium also is present in coal and is concentrated in the ash when coal is burned by power plants. The selenium can be leached from these residues and enter the aquatic environment.

Selenium chemistry is complex, and chemical forms vary in their environmental occurrence, biogeochemistry, and toxicity. In natural systems selenium is generally recognized to occur in four oxidation states: selenide (Se2-), elemental selenium (Se0), selenite (Se4+), and selenate (Se6+). Selenium commonly occurs as a mixture of several different chemical forms in surface waters. Soluble selenates are the predominant form under oxidizing conditions in alkaline soils commonly found in arid areas. Selenates are readily available to plants or they can be slowly reduced to selenites, which also can be taken up by plants and converted into organic forms. Selenite is the more common soluble form of selenium under reducing conditions and in acidic soils which occur more typically in higher-rainfall areas. Metal and organic selenides formed from selenite reduction are common in bottom sediments, but generally are insoluble and not readily bioavailable. Under aerobic conditions they can be oxidized to more bioavailable forms. Low waterborne selenium concentrations can reflect low mass loading, but also may reflect high biotic uptake of selenium. The common organic forms of selenium in plants

(incorporated from water and sediments) include selenomethionine, selenocysteine, dimethylselenide, and dimethyldiselenide.
Total recoverable selenium includes suspended detrital particulate matter (a function of biotic uptake) and thus more accurately reflects the total mass load of selenium in the system.

Selenium is similar and often an analog to sulfur in many biochemical reactions. When selenium is present at elevated dietary levels, it replaces sulfur in some metabolic pathways and thereby causes problems. Selenium is an essential component of the enzyme glutathione peroxidase, which, along with vitamin E, serves as an antioxidant to prevent metabolic damage to tissues. Selenium occurs in various chemical forms in plant and animal tissues, but bioavailability is greater from plant selenium than from animal foods. In general, the diet is the most important exposure pathway for vertebrate animals.

Selenium was recognized long ago as a cause of toxicity in domestic poultry and livestock. For fish and wildlife, selenium became much more of a concern in the 1970s and 1980s with the discovery of selenium bioaccumulation and severe impacts in fish and aquatic birds. During the early and mid-1980s, subsurface agricultural drainage waters from the San Joaquin Valley, California, were disposed of by discharging them to Kesterson Reservoir, which was a series of 12 shallow ponds totaling about 500 ha. Selenium concentrations in water entering the reservoir during 1983 to 1985 averaged about 300 μg/L, and aquatic plants and invertebrates contained greatly elevated concentrations of selenium. Almost all of the waterborne selenium was in the selenate form. Unlike boron and a number of other constituents, selenium concentrations *decreased* as the water flowed through the series of ponds and evaporated. Similarly, plants and animals as well as sediments in ponds nearer the inflow contained higher concentrations of selenium than those downstream. Thus, bioaccumulation by plants and animals removed substantial amounts of selenium from the water and deposited it into the sediments.

Many biogeochemical processes affect the cycling of selenium through different components of the environment, In wetlands, bacterially mediated oxidation-reduction reactions are the most important processes controlling selenium speciation, precipitation/dissolution, sorption/desorption, methylation, and volatilization. Selenium in oxygenated water entering a wetland is usually in the form of selenate but is converted slowly to selenite or elemental selenium as reducing conditions form. It can be further reduced to metal selenides or volatile methylated forms (primarily dimethylselenide). The metal selenides tend to be deposited in the wetland sediments, whereas volatile forms escape to the atmosphere. The changes described above can be important considerations in the wetting and drying cycles that occur in seasonal wetlands, as well as periodic draw-down of water levels in permanent wetlands. When submerged, especially where large amounts of organic material are present, selenium tends to be present in reduced (and less toxic) forms, and volatilization is favored. If the water level is lowered, the selenium becomes more oxidized and bioavailable. Thus, the selenium present in the wetland sediments and organic matter would become more likely to bioaccumulate into aquatic organisms soon after the wetland is reflooded than when it was previously flooded.

Numerous studies of selenium transformations, cycling, and volatilization in aquatic and terrestrial ecosystems have been reported in recent years. Not surprisingly, rates for these processes vary greatly, depending on temperature, moisture, organic carbon content of soil/sediment, selenium concentration and chemical form, and microbiological activity. Some selenium reduction processes and the bacteria that carry out the reactions have been identified. Selenate "respiring" bacteria can be cultured and columns developed for selenium removal. Although other reactions in the selenium metabolic pathway are not yet well known, it is clear that microbes, such as those involved in selenate reduction, are largely responsible for the changes that occur.

Plants vary widely in their ability to accumulate and volatilize selenium from contaminated wastewater, soils, and sediments. Under some circumstances, phytoremediation of these contaminated media may be a viable approach to reducing environmental exposures. It is unclear, however, whether the kinetics of these reactions are sufficient under a wide range of environmental variables to serve as an effective removal or cleanup strategy. Additionally, water-borne selenium can be accumulated by plants and animals living in the wetlands to levels that are harmful to aquatic organisms as well as birds that feed upon them. Because of bioaccumulation in the food chain and deposition to sediments, wetlands should not be used for phytoremediation of selenium-contaminated wastewater without conducting an ecological risk assessment to evaluate potential adverse effects to birds and other potentially exposed animals. This technology may be appropriate for waters containing moderate levels of selenium (perhaps up to 25 or 30 μg/L), but only if it is designed and managed to limit access by aquatic birds that would feed on plants and invertebrates in the wetland. However, at high waterborne concentrations of selenium, or with inadequate attention to design and management concerns, the wetland could present undesirable levels of exposure to birds.

Studies of the effects of selenium have focused mainly on domestic livestock and on fish and aquatic birds because those animals have been found to be sensitive to the adverse effects of excess selenium. In fish and birds, the early life stages (fish larvae/fry, bird embryos) are most sensitive, although lethal and sublethal adverse effects also occur in adult animals under field conditions in some areas. Teratogenic effects in fish larvae/fry and in bird embryos may lead to death of young that hatch, but a significant amount of mortality also may occur without visible developmental abnormalities and reduced hatching success.

Table 1. Background concentrations of selenium.

Medium	Selenium conc (mg/kg dw, except for water)
Freshwater	0.1-0.4 μg/L
Freshwater sediments	0.2-2.0
Plants: Freshwater algae:	0.1-1.5
Freshwater macrophytes:	0.1-2.0
Terrestrial plants	0.01-0.6
Invertebrates: Aquatic:	0.4-4.5
Terrestrial	0.1-2.5
Fish: Liver:	2-8
Other tissues	1-4
Reptiles/ Amphibians: Liver	2.9-3.6
Other tissues	1-3
Birds: Whole body.	<2
Muscle	1-3
Eggs	<5
Liver	<10
Feathers	.1-4
Whole blood	0.1-0.4
Mammals: Whole body	<1-4
Muscle	<1
Liver	1-10
Hair	<1-3
Milk	<0.05
Whole blood	0.1-0.5

Table 2. Selenium concentrations and biological effect thresholds.

Medium	No effect1	Level of concem2	Toxicity threshold3
Water (µg/L. total recoverable)	<1	1-2	>2
Sediment (mg/kg dw)	<1	1-4	>4
Diet (mg/kg/day, dw)	<2	2-3	>3
Waterbird eggs (mg/kg dw)	<3	3-6	>6
Fish, whole-body (mg/kg dw): cold-water species	<2	2-4	>4
Fish, whole-body (mg/kg dw): warm-water species	<3	3-4	>4

[1]Concentrations lower than this value produce no discernible adverse effects on fish or wildlife and are typical of background concentrations in uncontaminated environments.

[2]Concentrations in this range rarely produce discernible adverse effects but are elevated above typical background concentrations.

[3] Concentrations above this value appear to produce adverse effects on some fish and wildlife species.

Selenium accumulates in and disperses (depurates) from animal tissues fairly rapidly. Significant changes in tissue selenium status can occur within days, weeks, or months. Furthermore, the overt symptoms of even near-fatal selenium poisoning in adult birds and mammals can be reversed quickly if the source of selenium exposure is eliminated. By contrast, embryonic deformities caused by selenium poisoning are not reversible nor are some types of tissue damage in adult animals.

SELENIUM AND THE SALTON SEA

In order to evaluate the significance of selenium in the Salton Sea environment, the Salton Sea Science Office hosted a meeting of 13 selenium experts on March 11, 2003, in Sacramento, California. The goal of the meeting was to assess what is known about selenium in the Salton Sea and predict potential changes if any of the restoration proposals are implemented. Specific objectives were: 1) review what is known about selenium in the Salton Sea; 2) predict fate and impact of selenium resulting from the restoration scenarios; and 3) review technologies for removal of selenium from aquatic systems. The group documented current selenium levels in various components of the Salton Sea ecosystem and predicted levels for the various restoration proposals

General consensus of the group concerning selenium in the Salton Sea follows:

- Current inflows to the Sea contain low to moderate levels of selenium. However, because the inflow volume of water is so great, total selenium burden to the Salton Sea annually is equivalent to that of Kesterson Reservoir.

- The existing Sea appears to accommodate selenium. While most major ions increase by evaporative concentration in the Salton Sea, water borne selenium levels are lower in the Sea than the inflows. In contrast to major ions, selenium in water entering the Sea is diluted by the lower selenium concentration water in the Sea where it is continually removed by a variety biological processes

- Phytoplankton and algae take up selenium, but the absence of vascular plants in the Sea reduces its bioavailability. However, in-Sea food chains significantly bioaccumulate selenium for the large fish-eating birds and selenium levels in fish (human health advisories) and some birds are of concern.

- Selenium is currently bioavailable through invertebrate and fish consumption of bacteria and algae in the water column or in shallow sediments. However, the greatest portion of this selenium appears to become incorporated into deep anoxic sediments as the algae and bacteria die, becoming a detrital rain. These deep sinks have little or no biological activity, and thus for all practical purposes the selenium is biologically unavailable so long as the deep water and anoxic sediment conditions are maintained.

- Increased levels of selenium in most components of the ecosystem are expected as a result restoration proposals because of the reliance on desalination by reverse osmosis, or because of water transfers effectively reducing surface tailwater as a dilution factor

- Levels in the playas (exposed sediment areas) would be expected to be very high, in some cases >1000ppb in puddle water from irrigation practices or rainfall. Group consensus was that irrigation practices associated with vegetation for dust control would create selenium remobilization conditions far exceeding Kesterson Reservoir conditions.

- Situations with a fresh-water wetland component would support vascular vegetation and hence increase the bioavailability of selenium.
  For any foreseeable restoration scenarios, selenium treatment and removal would be required. Selenium treatment and removal technology, either chemically or biologically, is available and currently being tested.

- Tailwater reduction along drains tributary to the New and Alamo Rivers through conservation and water transfers will increase Se concentrations to roughly 12 ppb, then desalination could concentrate some of that inflow by a factor of 3, to

36 ppb. Selenium is of concern in the water column and sediments, but is also of greater concern in exposed sediments which may become fugitive dust, in the exposed sediment playas irrigated for vegetation establishment and especially in areas of the northern ½ of the seabed if exposed

The general conclusions are: 1) We would experience higher levels of selenium in most elements of the ecosystem for any restoration scenarios implemented; 2) some type of selenium treatment removal would be required; and 3) treatment and removal technologies are available for aquatic systems, but none are proven technologies scaled to the volume of water of the Salton Sea. Nanofiltration of waters post-desalination as well as combinations of nutrient reduction and selenium treatment appear promising. The environmental significance of selenium is a topic of ongoing discussion and debate. In particular, there are differences of opinion concerning waterborne concentrations of selenium that are protective for fish and wildlife, the relative importance of sediment vs. waterborne selenium in affecting aquatic biota, and the specific thresholds of selenium in the diet or eggs of birds at which reproduction is adversely affected.

Table 3. Observed selenium concentrations in the Salton Sea vicinity.

	CURRENT CONDITIONS mg/kg dry wt. except water
Water	1.5 µg/L
Sediment	$\bar{x}$ = 2.7 (0.2-11)
Vegetation	
Algae	0.5-2
Vascular	N.A.
Invertebrates	
Benthic	(1-9) med. 3.5
Water Column	(1-3) med 2.5
Fish	(6-24) med. 9
Birds	Stilts 50% of eggs > 6
Air Quality	N.A.
Humans	Se advisories for fish consumption (at threshold)

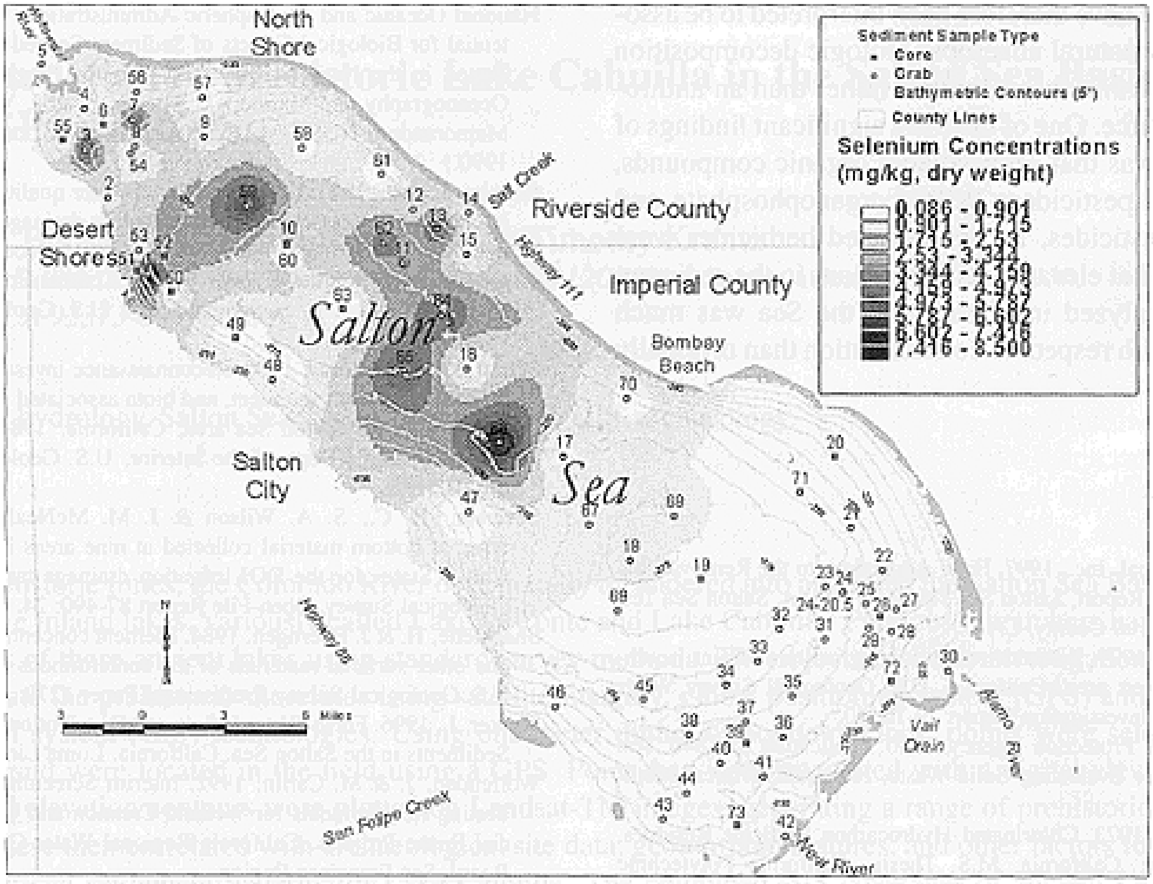

Figure 8. Selenium concentrations.

Sediment selenium concentrations of the Salton Sea (from Vogl R..and R. Henry. 2002. Characteristics and contaminants of the Salton Sea sediments. Hydrobiologia 473: 47-54

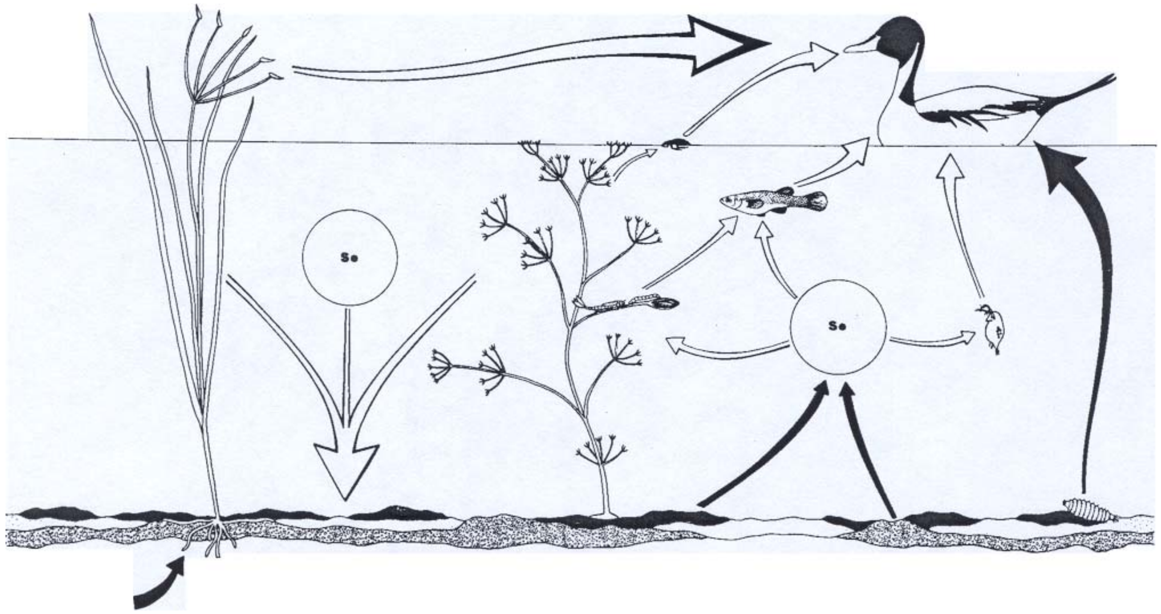

Fig. 1. A highly dynamic system: Biological, chemical, and physical processes cycle selenium into and out of the water, sediments, and biota. (solid arrows indicate pathways by which selenium is remobilized from sediments into the food chain.)

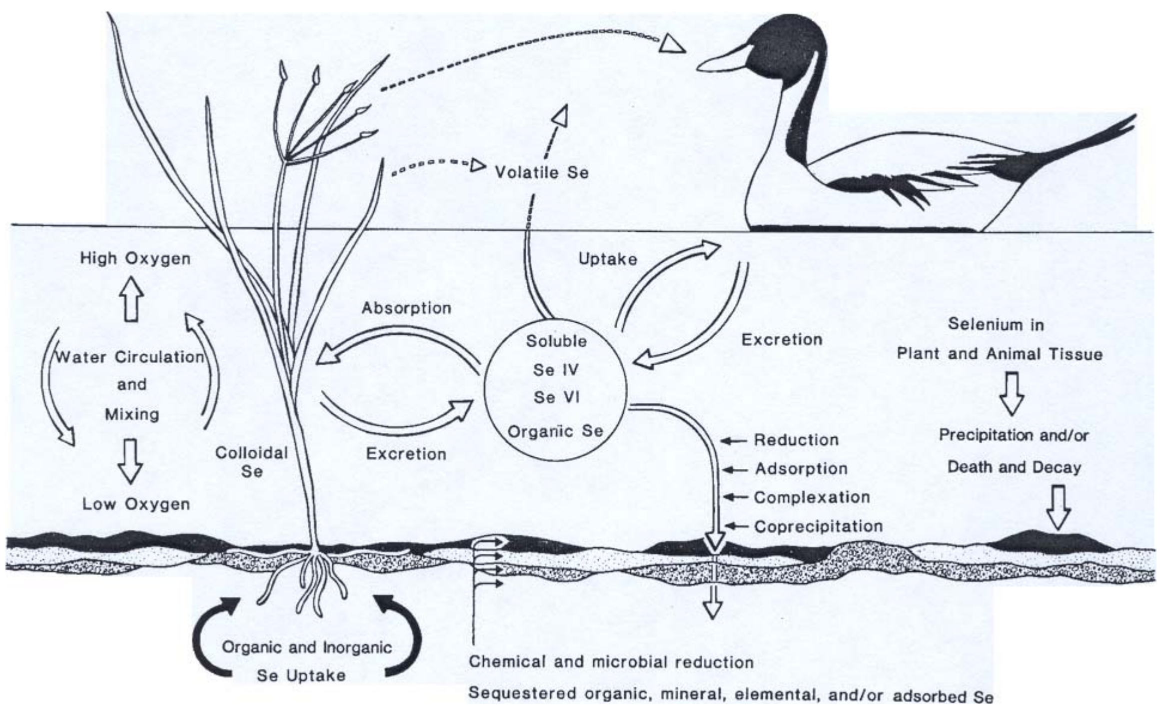

Fig. 2. Processes for the immobilization of selenium include chemical and microbial reduction, adsorption, coprecipitation, and deposition of plant and animal tissue; mobilization processes include uptake of selenium by rooted plants and sediment oxidation due to water circulation and mixing.

References. Information contained in this document, including tables and graphics, were taken and consolidated into an abbreviated format directly from the following publications and reports.

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